)LUMETRIC IODATE METHODS

BY

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BOOK DEPARTMENT

he CHEMICAL CATALOG COMPANY, *Inc.*

19 EAST 24th STREET, NEW YORK, U. S. A.

1926

Printed in the United States of America by
J. J. LITTLE AND IVES COMPANY, NEW YORK

PREFACE.

The object of this work was to bring together the various procedures and applications of the volumetric iodate methods in order that they may be more readily available for use. The methods have been employed in connection with routine analyses as well as with investigational work for about twenty years both here and abroad, but much more extensive use has been made of them within recent years.

The great stability of the potassium iodate solution and the remarkable sharpness of the end point of the titration are noteworthy. The non-interference of many kinds of organic matter makes these methods applicable to cases in which the permanganate method could not be satisfactorily used. The procedure can readily be adapted to the determination of many if not all of the substances to which Bunsen's process of distillation with potassium iodide and hydro-

chloric acid is applicable with much less expenditure of time and far simpler apparatus.

Throughout the text "hydrochloric acid" refers to the pure, concentrated acid (sp. gr. 1.18) unless otherwise stated.

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THE IODATE METHOD.

This method, which was first proposed in 1903 by L. W. Andrews (J. Am. Chem Soc., *25*, 756) for the titration of a number of reducing substances such as free iodine, iodides, arsenites, and antimonites in a very satisfactory manner, depends upon the formation of iodine monochloride and the disappearance of the iodine color imparted to an immiscible solvent such as chloroform or carbon tetrachloride. This method of titration has been found to be one of the sharpest and most uniform in its results. Since all of the iodine which remains during the latter part of the titration is collected in the small volume of immiscible solvent, the accuracy of the end reaction is extraordinary. When a titration has actually been completed there is no return of iodine color even after keeping the solution for a day.

The titration is made in glass-stoppered bottles or flasks of 250 or 300 cc. capacity in the presence

of hydrochloric acid. It is necessary to have at least 12 per cent of actual hydrochloric acid present in the titrated solution, otherwise hydrolysis of the iodine monochloride with the formation of iodine is liable to occur. With the directions given for the various titrations, it is not difficult to maintain the proper concentration of hydrochloric acid.

In a few cases, particularly where very small quantities of a substance are to be determined, it has been found advantageous at times to add a small quantity of iodine monochloride dissolved in hydrochloric acid and titrate the liberated iodine with the potassium iodate solution. This obviates any danger of over titrating the solution at the beginning, besides the use of iodine monochloride enables one to make these titrations much more rapidly. The addition of iodine monochloride to a solution before titration causes no change in the volumetric relations of the potassium iodate with the substance being estimated. However, it is essential that the iodine monochloride solution should be entirely free from either iodine or iodic acid. A convenient solution of iodine monochloride may be prepared as follows: Dissolve 10 grams of pure potassium

iodide and 6.44 grams of pure potassium iodat in 75 cc. of water, add 75 cc. of hydrochloric aci and 5 cc. of chloroform in a glass-stoppered bottl and adjust exactly to a very faint iodine colc (chloroform) by shaking and adding dilute potas sium iodide solution or potassium iodate as th case may require. When not in use, this solutio should be kept in a dark place.

It should be observed that iodate titration can be made in the presence of filter paper, alco hol, formaldehyde, acetic and other saturate organic acids, as well as many other kinds c organic matter.

For the preparation of standard iodate solu tions, it is recommended that normal potassium iodate be employed because it is a very stabl salt of constant composition and it can be readil purchased in a pure condition. Before using th salt it should be dried at about 120° C to insur its freedom from moisture. Unlike most volu metric solutions, the iodate solution is mad standard by simply dissolving the calculate weight of the salt in distilled water and dilutin to the proper volume. This is best done b weighing the salt accurately on a watch glass an transferring it by means of a camel's hair brus

of hydrochloric acid. It is necessary to have at least 12 per cent of actual hydrochloric acid present in the titrated solution, otherwise hydrolysis of the iodine monochloride with the formation of iodine is liable to occur. With the directions given for the various titrations, it is not difficult to maintain the proper concentration of hydrochloric acid.

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directly into the dry graduated flask. The flask is filled half full with water and gently rotated until the salt is completely dissolved before the solution is brought to the final volume. The solution will keep its strength indefinitely. Solutions kept for ten years showed no measurable change and the only precaution taken was to prevent evaporation. Should there be any uncertainty in regard to the purity of the potassium iodate at hand or in connection with the relations of the volumetric apparatus, it would be advisable to standardize the solution Some analysts employ a standard solution of potassium iodide for cases in which a solution has accidentally been overtitrated by potassium iodate. A small measured volume of the potassium iodide solution, which has previously been standardized by titrations with the iodate solutions, is added and after shaking the solution, the titration with potassium iodate is continued. The proper deduction is to be made for the potassium iodide used.

It should be observed that since both iodine and potassium iodide react with potassium iodate in the presence of hydrochloric acid, the iodate method cannot be employed for the standardization of iodine solutions. The equations for the

:tions of potassium iodate with potassium ide and iodine in the presence of 12 per cent nore of hydrochloric acid are as follows:

$$\text{ΚI} + KIO_3 + 6HCl = 3KCl + 3ICl + 3H_2O$$
$$I_2 + KIO_3 + 6HCl = KCl + 5ICl + 3H_2O$$

THE DETERMINATION OF ANTIMONY

The method is based on the titration of antimonious compounds with potassium iodate in the presence of 15 to 20 per cent of actual hydrochloric acid according to the following equations:

$$2SbCl_3 + KIO_3 + 6HCl = 2SbCl_5 + KCl + ICl + 3H_2O$$

$$2H_3SbO_3 + KIO_3 + 2HCl = 2H_3SbO_4 + KCl + ICl + H_2O$$

The method was tested by dissolving weighed quantities of Kahlbaum's pure antimony in concentrated sulphuric acid, taking precautions to heat the solution until all of the sulphur dioxide was volatilized. After the addition of water and hydrochloric acid as directed below, the solution was titrated with potassium iodate, 1 cc. of which corresponded to 0.00400 gram of antimony. The following results were obtained:

Sb Taken Gram	KIO_3 Used Cc	Sb Found Gram
0.1000	24.85	0.0994
0.1000	24.90	0.0996
0.0490	12.20	0.0488

The Determination of Antimony in Alloys.

The following method is particularly adapted to "hard leads," solders, type metal, and similar alloys. The method is satisfactory because it is not interfered with by copper and iron, which frequently occur in small quantities in these alloys and because it is rapid as well as accurate.

Take 0.1 to 1.0 gram of the alloy (depending upon the quantity of antimony present) in the form of drillings or chips in a 200 cc. Erlenmeyer flask. Add 10 cc. of concentrated sulphuric acid, cover flask with an inverted porcelain crucible cover, and heat until the alloy is completely decomposed. Boil the solution gently, after the lead sulphate becomes white, until the sulphur dioxide is entirely expelled. Allow the solution to cool to room temperature, add 15 cc. of cold water and 15 cc. of 1:1 hydrochloric acid. Shake thoroughly, cool to room temperature, and filter the lead sulphate on a Gooch crucible, washing with small quantities of 1:1 hydrochloric acid. Transfer the filtrate to a 250 cc. glass-stoppered bottle, add 15 cc. of hydrochloric acid, cool again if necessary, and add 6 cc. of chloroform. Then titrate

with the potassium iodate solution. After the disappearance of the iodine color from the chloroform allow the solution to stand for about 10 minutes, shake and observe whether the chloroform shows any iodine color. If no color is present, the titration is completed. To make a second titration most of the liquid may be poured off, leaving the chloroform ready for use. In the case of alloys which contain very small quantities of antimony, add 5 cc. of a hydrochloric acid solution of iodine monochloride before titration. Shake and allow the solution to stand 5 minutes. Then titrate the iodine liberated by the reaction of the antimonious salt and the iodine monochloride with potassium iodate solution. The use of iodine monochloride does not alter the value of the potassium iodate solution in terms of antimony as calculated from the equation given above. The use of iodine monochloride solution enables one to complete these titrations quickly in addition to avoiding the danger of over titration of the antimony at the beginning when only small quantities are present. To prepare the iodine monochloride solution, dissolve 10 grams of potassium iodide and 6.44 grams of potassium iodate in 75 cc. of water, add 75 cc. of hydrochloric

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ssium iodide or iodate as the case may re-
e. This solution should be prepared only
chemicals of high purity and when the solu-
is not in use it should be kept in a dark
e, otherwise it will require frequent readjust-
ts by further addition of potassium iodate.
ie following results were obtained with a
ber of alloys:

(1 cc of KIO_3 = 0 00400 gram Sb)

Weight Taken	Cc KIO_3 Used	Per-cent of Sb	Percent of Sb by Thiosul-phate Method
0.2000	6 70	13 40	13 43
0 2000	6.70	13 40	—
0.2000	6 00	12 00	12 07
0.2005	6 03	12 03	—
1.0000	2.70	1.08	1.04
1 0000	2.70	1 08	—
1 0000	2 40	0.96	0 96
0.5000	2 85	2.28	2.32
1 0000	2 80	1 12	1.16

should be observed that when more than
. of iodate solution are required for a titra-

tion it is necessary to use additional hydrochloric acid before reaching the end point when the acidity of the solution should not be less than about 12 per cent of actual hydrochloric acid for the prevention of the hydrolysis of the iodine monochloride with the formation of free iodine.

The time required for an analysis is about an hour.

Alloys containing antimony may be decomposed with hydrochloric acid and potassium chlorate. The larger part of the acid is neutralized with ammonium or sodium hydroxide and the antimony pentachloride is reduced with sulphur dioxide. The sulphur dioxide is completely removed by boiling the solution. After the solution has cooled, slightly less than an equal volume of hydrochloric acid is added. The solution cooled to room temperature may be titrated directly or after the addition of 5 cc. of iodine monochloride solution as previously described.

Arsenic is rarely present in appreciable quantities in the alloys under consideration, but it is to be noted that if present it would be titrated with the antimony. In a case where an alloy contains an appreciable quantity of arsenic it is best to conduct the procedure exactly as directed

: far as filtering off the lead sulphate and wash-g it with 1:1 hydrochloric acid. Then pass in ⁄drogen sulphide to precipitate the arsenic, pass r through the solution for half an hour to re-ove the hydrogen sulphide and oxidize any iron at may be present, filter, wash with 1:1 hydro-ıloric acıd, and titrate the filtrate in the usual anner. This process was tested by the use of loys mixed with known quantities of pure etallıc arsenic with the following results:

ılloy Taken Gram	As Taken	Per Cent Sb Found	Per Cent Sb ın Alloy
0 5000	0 0050	4 72	4 72
0 9560	0 0118	4 77	4 72
0 2000	0 0460	12 00	12 00
0.2000	0 0520	12 10	12 00
1 0000	0 0097	1 04	1.08

THE DETERMINATION OF ARSENIC.

Arsenic can be determined in the same manner as antimony except that not over 20 per cent of actual hydrochloric acid should be present at the end of the titration with potassium iodate solution, otherwise the end reaction is not sharp. The reactions of arsenious compounds with potassium iodate may be represented by the following equations:

$$As_2O_3 + KIO_3 + 2HCl = As_2O_5 + ICl + KCl + H_2O$$

$$2H_3ASO_3 + KIO_3 + 2HCl = 2H_3AsO_4 + ICl + KCl + H_2O$$

$$2AsCl_3 + KIO_3 + 5H_2O = 2H_3AsO_4 + ICl + KCl + 4HCl$$

Arsenic in arsenical lead can be readily determined according to the directions given for antimony in solders, etc. In the case of alloys which contain both antimony and arsenic, the arsenic may be separated as sulphide as directed

under the determination of antimony. When the arsenic is separated as sulphide, the precipitate is dissolved in warm ammonium hydroxide and boiled with 30 to 50 cc. of 3 per cent hydrogen peroxide for 10 minutes. The solution is acidified with hydrochloric acid and after reducing the arsenic with sulphur dioxide, the solution is boiled until free from sulphur dioxide because it will react with potassium iodate. When the solution has cooled to room temperature, add two-thirds its volume of hydrochloric acid and titrate with potassium iodate solution in the usual manner.

Determination of Arsenic in Insecticides.

For the determination of arsenious oxide in Paris green or other arsenite from 0.15 to 0 4 gram of the sample, depending upon the amount of arsenic present, was weighed directly into a 250 cc. or 300 cc. glass-stoppered bottle. Thirty cubic centimeters of hydrochloric acid, 20 cc. of water and 6 cc. of chloroform were added. The titration was made by adding the potassium iodate solution, rapidly at first, while shaking the bottle so as to give the contents a gyratory motion. When the iodine which is liberated during the first part of

the titration has largely disappeared from the solution, the stopper is inserted and the contents of the bottle are given a thorough shaking. From this point the titration is continued cautiously, shaking the stoppered bottle after each addition of iodate solution, until the iodine color of the chloroform has disappeared, which marks the end point. It is customary to allow the titrated solution to stand five minutes, then if after shaking again any color is observed in the chloroform it is expelled with the smallest possible quantity of iodate solution. It is very important to shake the solution more thoroughly the nearer the end point is approached, otherwise the solution may be overtitrated. Furthermore, it has been found that the larger the volume of the solution being titrated, the more shaking is required to bring the chloroform carrying the iodine in contact with the potassium iodate. The entire determination, after a little practice with the iodate titration, can usually be completed in about fifteen minutes. It should be observed that the strength of the hydrochloric acid in which the titration is made is of much importance. The acidity at the end of the titration should not be less than 12 per cent of actual hydrochloric acid, so as to

revent the hydrolysis of the iodine monochloride.)n the other hand, the acidity should not exceed 0 per cent, otherwise the reaction proceeds very lowly. It is a simple matter to keep the acid rithin the required limits. In order to facilitate alculations, and also if it is desired to weigh ırger quantities of the insecticide, a gram or ıctor weight may be employed. In such cases , would be recommended that the sample be issolved in 200 cc. of hydrochloric acid, and ıade to 500 cc. volume; then to each 100 cc. liquot, 10 cc. of hydrochloric acid should be dded to maintain the proper acidity during the itration. Using a potassium iodate solution of rhich 1 cc. = 0.00330 gram As_2O_3, the results on . 22 were obtained.

The results obtained by the iodate method gree closely with those of the modified Hedge rocedure.

In order to apply the iodate titration to the etermination of total arsenic in any arsenical ısecticide or fungicide the official distillation rocess of the Association of Official Agricultural hemists (J. A. O. A. C., 1915, 1916 and 1917) as employed and the distillation apparatus was rranged as follows:

Insecticide	Gram Taken	Cc of KIO_3 Used	Percentage As_2O_3 Found: Iodate Method	Percentage As_2O_3 Found: Hedge's Modified Method
Paris Green No. 12542	0 1287	22.20	56 92	57.05
" " " "	0 1166	20 10	56 88	56.93
" " " "	0.1207	20.80	56 87	—
" " " "	0 1325	22 85	56 90	—
" " " 12489	0 1794	33 92	56 72	56 75
" " " "	0 1533	28 95	56.65	—
" " " "	0 1124	21.23	56 67	—
" "	0 1689	31.22	56 80	56.85
" "	0 1851	35.05	56.81	—
Zinc Arsenite	0.2088	26 25	41 68	41.79
" "	0.2998	41 65 (a)	41 68	41 87
Bordeaux Zinc Arsenite	0 1984	20 60	34.21	34.22
" " "	0 1788	18 50	34.14	—
" " "	0.2000	20 72	34 19	—
Bordeaux Paris Green	0 3179	30 60	31 76	31.70
" " "	0.2279	21 90	31 71	31 61
" " "	0 1912	18 40	31 74	—

(a) KIO_3 solution with 1 cc = 0 003000 gram As_2O_3

An 8 oz. distilling bulb, provided with a long-stem 50 cc. dropping funnel, was connected to a 24-inch Liebig condenser. The outlet of the condenser was connected to a 500 cc. Erlenmeyer flask with a bent glass tube which extended through a 3-hole rubber stopper for about 4 inches. The middle hole carried a safety tube 18 inches long which extended within half an inch of the bottom of the flask. The third hole carried a bent tube which extended through a 2-hole stopper to within half an inch of the bottom of the second 500 cc. flask. Another bent tube just passing through the second hole of this stopper was arranged so that it dipped into the 50 cc. of water placed in a 250 cc. Erlenmeyer flask which served as a trap. During the distillation the first two Erlenmeyer flasks were surrounded by cracked ice in a pan. The distillation flask rested in a circular hole cut through a heavy sheet of asbestos board. A wire gauze was placed under the asbestos board. Before starting the distillation 50 cc. of water was placed in the first receiver, 100 cc. in the second receiver, and 50 cc. in the third. The sample taken for analysis was weighed directly into the dried distilling bulb and 5 grams of cuprous chloride was added. This

was followed by 100 cc. of hydrochloric acid, which washed any material sticking to the neck into the bulb. Care must be taken that none of the sample of cuprous chloride enters the outlet tube of the distilling bulb. When the volume in the distillation bulb is reduced to about 40 cc., 50 cc. more of the acid is added through the dropping funnel and the distillation is continued until the volume is again reduced to about 40 cc. Then 25 cc. more of the acid is added. The distillation is finished when the contents of the distillation flask are reduced to not more than 20 cc. This procedure insured the distillation of all the arsenic. After the distillation was completed, the condenser and connecting tubes were thoroughly rinsed into the receivers. The contents of the first two flasks were transferred to a 500 cc. graduated flask. These flasks were rinsed several times, using the entire contents of the third flask, which served as a trap. Then each flask was rinsed again with a small quantity of water. All of the rinsings were added to the graduated flask. Before diluting to the mark, the solution in the 500 cc. flask was warmed to room temperature. After diluting and thorough mixing of the solution, an aliquot of 100 cc. was removed and placed

ın the titration bottle along with 6 cc. of chloroform and titrated with the potassium iodate solution as described above. If more than 25 or 26 cc. of the iodate solution were required, 10 to 15 cc. hydrochloric acid were added before finishing the titration in order to maintain the proper acidity. For comparison, aliquot portions were titrated with standard iodine solution after neutralization of the hydrochloric acid. It was found preferable to neutralize the larger part of the acid with 25 per cent sodium hydroxide instead of neutralizing all of the acid with sodium bicarbonate as recommended. This is liable to cause some loss of arsenic on account of the violent evolution of carbon dioxide.

On account of the physical property of the powdered insecticides which causes them to adhere to glass, making their transference difficult, it was found preferable to weigh portions of the samples by difference from specimen tubes rather than attempt to weigh, for example, an exact 0.5 gram. The results of the test analyses by the iodate method given above show excellent agreement with those obtained by the official A. O. A. C. method. This iodate method is not only more rapid, but is simpler than the iodine titration.

The very definite and remarkably sharp end point, the great stability of the potassium iodate solution together with the ease with which it can be prepared, all recommend its use for the accurate determination of arsenious oxide or total arsenic in insecticides, fungicides and other substances.

Using a potassium iodate solution of which 1 cc. = 0.003000 gram As_2O_3, the following results were obtained:

Insecticide	Gram Taken	Cc. of KIO_3 Used for 100 Cc Aliquot	Total Arsenic as As_2O_3 Iodate Method Per Cent	Total Arsenic as As_2O_3 Iodine Method Per Cent
Paris Green 12542 .	0 4782	18 20	57 06	57 15
" " "	0 6266	23 65	56 62	56 64
" " "	0 5745	21 66	56 56	56 57
" "	0 5888	23 33	56 88	56 92
" "	0 6042	22 85	56 86	56 80
Bordeaux Paris Green	0 5865	12 55	32 09	32 06
Bordeaux Paris Green	0 6520	13 95	32.09	—
Lead Arsenite—Arsenate	0 4052	7 20	26 65	—
Lead Arsenite—Arsenate .. .	0.4945	8 80	26 70	26 71
Zinc Arsenite	0 5486	15 40	42 10	42 21
Bordeaux Zinc Arsenite	0 6106	14.00	34 39	34 37
Bordeaux Zinc Arsenite	0.6193	14.18	34.34	34.38

Ihe method is based upon the titration of ɔrous thiocyanate with potassium iodate in the ɜsence of strong hydrochloric acid and a chloro-m indicator. The reactions taking place may represented by the following equations:

$$uSCN + 2KIO_3 + 4HCl = 2CuSO_4 + 3KCl + 2HCn + ICl + I_2 + H_2O$$

$$_2 + KIO_3 + 6HCl = KCl + 5ICl + 3H_2O \quad \text{or}$$

$$4CnSCN + 7KIO_3 + 14HCl = 4CuSO_4 + 7KCl + 4HCN + 7ICl + 5H_2O$$

In order to test the method a solution was pre-red which contained 10.706 grams of potassium late in 1000 cc. and 1 cc. = 0.001817 gram of ι. Measured volumes of a copper sulphate solu-n of known strength were precipitated with lphurous acid and ammonium thiocyanate, .ered sometimes on asbestos, sometimes on per, washed with water, and the filters contain-g the precipitates were transferred to 250 cc.

glass-stoppered bottles. A mixture of 30 cc. of hydrochloric acid and 20 of water along with 6 cc. of chloroform were added and the precipitates were titrated with the following results:

Copper Taken Gram	KIO_3 Used Cc.	Copper Found Gram
0 0486	26 7	0 0485
0.0486	26 8	0 0486
0 0388	21 3	0 0387
0 0486	26 7	0 0485
0 0486	26 9	0 0488

In applying the method to ores, lead and antimony, if not removed, will produce high results, but both of these metals are removed (to such an extent at least that they do not interfere in the slightest degree) by the evaporation with sulphuric acid in the process to be described Silver also must be removed.

The Determination of Copper in Ores.

To 0 5 gram of the ore in a 6-ounce flask, add 6 to 10 cc. of strong nitric acid, and boil gently, best over a free flame, keeping the flask in constant motion and inclined at an angle of about

45°, until the larger part of the acid has been removed. If this does not completely decompose the ore, add 5 cc. of hydrochloric acid and continue the boiling until the volume of liquid is about 2 cc. Cool somewhat, add gradually and carefully 6 cc. of concentrated sulphuric acid, and continue the boiling until sulphuric acid fumes are evolved copiously. Allow to cool, add 25 cc. of water, heat to boiling, and keep hot until the soluble sulphates have dissolved. Filter into a perfectly cleaned beaker, and wash the flask and filter thoroughly with cold water. With ores containing appreciable quantities of silver, a few drops of hydrochloric acid should be added before the filtration, but not enough to dissolve any considerable amounts of the lead sulphate or antimonic oxide that may be present. Nearly neutralize the filtrate with ammonia and add 10 to 15 cc. of a strong solution of sulphurous acid. Heat almost to boiling and add 5 to 10 cc. of a 10 per cent solution of ammonium thiocyanate, according to the amount of copper present. Stir thoroughly, allow the precipitate to settle 10 to 15 minutes, filter on paper, and wash with hot water until the ammonium thiocyanate is removed. Place the filter with its contents in the

titration bottle and by means of a piece of moist filter paper transfer into the bottle also any precipitate adhering to the stirring rod and beaker. Add 30 cc. of hydrochloric acid, 20 cc. of water, and 5 or 6 cc. of chloroform.

During the first part of the titration, add the potassium iodate solution rapidly while rotating the bottle in order to keep the contents mixed. When the iodine which is liberated during the first stage of the reaction has disappeared from the solution, insert the stopper and shake thoroughly. From this point continue the titration slowly, shaking the closed bottle thoroughly after each addition of potassium iodate until the iodine color has disappeared from the chloroform indicator, which marks the end point.

In order to make another titration, it is not necessary to wash the bottle or throw away the chloroform. Pour off two-thirds or three-fourths of the liquid in order to remove most of the pulped paper, too much of which interferes with the settling of the chloroform globules after agitation; add enough properly diluted acid to make about 50 cc. and proceed as before. In this case, where iodine monochloride is present at the outset, the chloroform becomes strongly colored with

dine as soon as the cuprous thiocyanate is added, ıt this makes no difference with the results of e titration.

In the following experiments weighed quanti- ɜs of pure copper were put through the above ›urse of analysıs in the presence of antımony, ıd in some cases lead also:

(1 cc KIO_3 sol = 0 003610 gram Cu)

Copper Taken Gram	Antımony Gram	Lead Gram	KIO_3 Used Cc	Copper Found Gram
0 1136	0 06	—	31 35	0 1131
0 0691	0 06	—	19 05	0.0688
0 0733	0 06	Present	20.30	0 0733
0 0673	0 06	"	18 75	0 0677
0 0650	0 06	—	18.08	0.0651
0 0486	0 03	—	13.50	0 0487
0 0486	0 03	—	13 48	0 0486

Several ores, sulphides, some of which con- ιined lead or antimony, were analyzed by this ιethod in order to compare the results with other ιethods.

So far as ease and rapidity are concerned, an ɑalysis of a copper ore has been made in one our including weighing and calculation, by the

iodate method. It is recommended that for convenience some multiple of 5 892 grams of potassium iodate per liter be employed which gives exact milligrams of copper per cubic centimeter, according to the multiple taken. For example, with 11.784 grams of KIO_3 per liter, 1 cc. = 0.002000 gram of copper.

1 (cc KIO_3 sol = 0 001817 gram Cu)

No.	Ore Taken Gram	KIO_3 Used Cc	Copper Found Per Cent	Copper by Other Methods Per Cent
1	0 5000	32 20	11 70	11 71 Electrolytic
2	0 5000	39 80	14 46	14 50 "
3	0 2000	22 90	20 80	20 70 Iodide
4	0 2000	21 08	19 15	19 02 Electrolytic
4	0 2000	21 10	19 16	—
5	0 2000	20 80	18 89	18 80 Iodide

Determination of Copper in Alloys.

For the analysis of alloys such as brass and bronze which contain a high percentage of copper, it is recommended that a solution containing 23.568 grams of potassium iodate in 1000 cc., 1 cc. = 0.004000 gram of Cu, be used. When desired the tin and lead may be separated

and determined in the customary manner, otherwise the analysis is conducted as described above for the determination of copper in ores. In cases where the zinc is to be precipitated after the removal of copper, as zinc mercuric thiocyanate, the sulphuric acid should not be neutralized as directed with ammonia, but with 20 per cent sodium hydroxide, in order to avoid an excessive quantity of ammonium salts which interfere with the quantitative precipitation of the zinc.

Determination of Copper in Insecticides.

From 0.2 to 0.5 gram of insecticide, depending upon the amount of copper present, was weighed into a No 2 beaker. The powder was thoroughly moistened with 10 cc. of water. About 5 cc. of sulphuric acid (1 3) was added and the solution was warmed to facilitate the decomposition. It was observed in some cases that a small quantity of difficultly soluble material remained even after heating. No attention need be paid to this, as it caused no interference with the accuracy of the method. When the sample was completely decomposed, the larger part of the free sulphuric acid was neutralized with 1:1 ammonium

hydroxide. The solution which should now have a volume of 30 to 40 cc. was heated almost to boiling and treated with 10 cc. of strong sulphur dioxide water. Then 5 to 10 cc. of a 10 per cent solution of ammonium thiocyanate was added and the solution was stirred for 2 minutes. The precipitate was allowed to settle for 15 minutes or longer before filtration. The cuprous thiocyanate was filtered on a close filter paper and washed with warm water until the soluble thiocyanate was removed. Excessive washing should be avoided. Sometimes the cuprous thiocyanate will run through the filter. In such cases continue the filtration until the filter has become clogged and the filtrate is running clear, then refilter. The filter containing the precipitate was transferred to the titration bottle and the titration was made as previously described. The results on p. 35 were obtained using a solution which contained 11.784 grams of potassium iodate in 1000 cc.; 1 cc. = 0.00200 gram of copper.

When more than 45 cc. of potassium iodate solution was required, 5 or 10 cc. more of hydrochloric acid should be added before continuing the titration in order to prevent any hydrolysis of the iodine monochloride.

Insecticide	Gram Taken	Cc KIO$_3$ Used	Per Cent of Copper	Per Cent of Copper by Iodide Method
'aris Green ...	0 1866	22 70	24 33	24.34
" " ...	0.2667	32 55	24 41	24 45
" " ...	0 2038	24.20	23 75	23 79
ordeaux Paris Green	0 5121	48.18	18.81	18.80
ordeaux Zinc Arsenite	0.4574	21 20	9 27	9 29

These and many other test analyses show that he iodate method gives very satisfactory results nd that it is to be recommended for the deterination of copper in insecticides.

In order to test the method, weighed portions of pure hydrazine sulphate were placed in the titration bottles. To each was added a mixture of 30 cc. of hydrochloric acid, 20 cc. of water and 6 cc. of chloroform. Then the potassium iodate solution was run in gradually, with shaking between the additions, until the chloroform, after increasing and then diminishing in color, was just decolorized. A solution was used which contained 3 567 grams of potassium iodate in 1000 cc. According to the equation $N_2H_4.H_2SO_4 + KIO_3 + 2HCl = N_2 + ICl + KCl + H_2SO_4 + 3H_2O$, 1 cc. $= 0.000534$ gram N_2H_4, or 0.002169 gram $N_2H_4.H_2SO_4$.

The following results were obtained:

No.	$N_2H_4.H_2SO_4$ Gram Taken	KIO_3 Used Cc	$N_2H_4.H_2SO_4$ Gram Found	Error Gram
1	0 0487	22.50	0 0488	+0 0001
2	0 0434	19 90	0 0432	—0 0002
3	0 0589	27 30	0 0592	+0 0003
4	0 0472	21 90	0 0475	+0 0003
5	0 0986	45 65	0 0990	+0 0004
6	0 1060	49 00	0.1063	+0 000[illegible]

method was tested further by titrating the ng sparingly soluble double-salts:

bstance	Gram	KIO_3 Used Cc	N_2H_4 Per Cent	Calculated Per Cent
$N_2H_4)_2.H_2SO_4$	0 1163	43.20	19.83	19 81
	0 0880	32 60	19 77	"
$N_2H_4)_2$ H_2SO_4	0 1591	51 25	17.21	17 29
	0 1396	45 10	17 25	"
$N_2H_4)_2.H_2SO_4$	0 0692	26 30	20 29	20 23
	0.0890	33 80	20.28	"
$N_2H_4)_2.H_2SO_4$	0 1308	49 20	20 09	20 20
	0 1059	39 70	20 02	"

above titrations were conducted in the nanner as in the case of the simple hydra- ılphate. It was observed that the nickel ·acted very slowly, apparently on account ıcult solubility, while the other compounds .itrated about as readily as the hydrazine te alone.

ᵓas found that phenyl hydrazine could not ısfactorily titrated with potassium iodate, ' because the color due to the presence of decomposition products was dissolved by loroform indicator and this interfered with

the observation of the end point. In recent years it has been found possible in a number of instances to extract the troublesome color with a solvent such as chloroform, leaving the substance to be titrated in the aqueous solution. After separating the colored chloroform, the titration is made in the usual manner. Although no experiments have been made with phenyl hydrazine it is probable that the color can be similarly removed so that it can be titrated.

DETERMINATION OF PEROXIDE IN LITHARGE.

'he method which was devised by L. S. Dean ased on adding an excess of potassium iodide .he form of a standard solution to a weighed tion of litharge and after the addition of rochloric acid, the potassium iodide not de-ıposed by the lead peroxide is titrated in the al manner with potassium iodate solution, ıg chloroform on carbon tetrachloride as an cator. The potassium iodide solution is ıdardized by titration with potassium iodate ıtion in the presence of strong hydrochloric l. The equations of the reactions are as ›ws:

$$PbO_2 + 2KI + 8HCl = 2PbCl_2 + 2KCl + 2ICl + 4H_2O$$

$$KI + KIO_3 + 6HCl = 3KCl + 3ICl + 3H_2O$$

omparison of the results obtainable by the

iodate method and those with the well-known Bunsen method are as follows:

Iodate Method (% of PbO_2)	31.95	32.00	5.10	5.14	10.50
Bunsen Method (% of PbO_2)	32.09	32.05	5.22	5.20	10.56

These results show that the iodate method is accurate. It should be observed that any organic matter which may be present does not interfere with the iodate titration. It is very important to use sufficient hydrochloric acid so that at least 12 per cent of the actual acid will be present at the end of the titration, in order to prevent the hydrolysis of the iodine monochloride. This method can be employed for the analysis of other similar peroxides, dichromates, permanganates, etc. Some of the equations of these reactions are as follows:

$$3KI + K_2Cr_2O_7 + 14HCl = 5KCl + 2CrCl_3 + 3ICl + 7H_2O$$

$$5KI + 2KMnO_4 + 16HCl = 7KCl + 5ICl + 2MnCl_2 + 8H_2O$$

$$KI + MnO_2 + 4HCl = KCl + ICl + MnCl_2 + 2H_2O$$

$$3KI + 2CrO_3 + 12HCl = 3KCl + 2CrCl_3 + 3ICl + 6H_2O$$

$$KI + BaO_2 + 4HCl = KCl + ICl + BaCl_2 + 2H_2O$$

This method was successfully applied by L. W. ndrews (J. Am. Chem. Soc., *25*, 756) to the de- rmination of chlorates and chromates.

THE DETERMINATION OF MERCURY.

This method is based upon the precipitation of mercury from mercuric compounds in neutral or acid solutions with a reagent which contains 39 grams of ammonium thiocyanate and 29 grams of zinc sulphate per liter of solution. The precipitate of mercuric zinc thiocyanate after filtration is titrated with potassium iodate solution in the presence of strong hydrochloric acid. The reaction which takes place during the titration is according to the following equation:

$$HgZn(SCN)_4 + 6KIO_3 + 12HCl = HgSO_4 + ZnSO_4 + 2H_2SO_4 + 6ICl + 4HCN + 6KCl + 2H_2O$$

In order to get a quantitative precipitation of the mercuric zinc thiocyanate there should not be more than 5 per cent of free acid present in the solution before the addition of the precipitating reagent. Also it should be observed that in cases where larger quantities of acid are required for

the solution of a substance the excess of acid should be neutralized with sodium hydroxide instead of ammonia because an excessive quantity of ammonium salts exerts a solvent action upon the precipitate of the double thiocyanate. In applying this method to the determination of mercury, it should be observed that cadmium, cobalt, copper, bismuth, manganese and mercurous compounds give insoluble double thiocyanates. Nickel in small quantities does not interfere appreciably with the method.

In order to test this method measured quantities of a standard mercuric chloride solution were taken in perfectly clean small beakers. Each solution was treated with 25 cc. of the reagent described above and the solution was diluted so that the final volume would be about 75 cc. The solutions were vibrated by striking the sides of the beakers with a stirring rod to facilitate the separation of the crystals. After the solutions have stood for about five minutes, they were briskly stirred with a glass rod, previously moistened with water, for about a minute. This treatment permitted the rod to be easily rinsed free from the precipitate so that it could be removed from the beaker. The solutions were allowed to

stand an hour or longer before filtration. The precipitates were collected on 7 cm. filter papers, placed in small Hirsch porcelain funnels using gentle suction and were washed four or five times with a solution which contained 5 cc. of the thiocyanate reagent and 450 cc of water on account of the solubility of mercuric zinc thiocyanate in pure water. When the filters had drained, the suction was stopped The filter papers containing the precipitates were carefully removed from the funnels and were folded so that they could be placed in 8 oz. glass-stoppered titration bottles. A cooled mixture of 35 cc. of hydrochloric acid and 10 cc. of water, along with 6 or 7 cc. of chloroform, was added to one of the titration bottles containing mercuric zinc thiocyanate, because it is best to titrate immediately after the addition of acid to the precipitate. During the first part of the titration the potassium iodate solution is added rapidly while rotating the bottle in order to keep the contents mixed. When the iodine which is liberated during the first stage of the reaction has disappeared from the solution, the stopper is inserted and the contents of the bottle are thoroughly mixed by shaking for about half a minute. From this point the

tration is continued slowly, shaking the closed
ottle thoroughly after each addition of potas-
um iodate solution, until the iodine color has
isappeared from the chloroform which marks
ie end point. If more than 50 cc. of the potas-
um iodate solution are required, 10 to 15 cc.
iore of concentrated hydrochloric acid are added
efore proceeding with the titration. The follow-
ig results were obtained using a solution which
ontained 39 2882 grams of KIO_3 in 1000 cc., 1 cc.
eing equivalent to 0 006133 gram of mercury.
'or general use, a solution containing 19.2191
rams of KIO_3 in 1000 cc, 1 cc. of which is equiva-
ent to 0.00300 gram of mercury, is recommended.

No	Hg Taken Gram	KIO_3 Used Cc.	Hg Calculated Gram
1	0 1006	16 40	0 1006
2	0 0805	13 15	0 0806
3	0 0503	8 25	0 0506
4	0 0805	13 15	0 0806
5	0 0905	14 70	0 0902
6	0 0201	3 30	0 0202
7	0 0825	13 45	0 0825
8	0 0945	15 40	0 0945

These analyses show that the method gives
ery satisfactory results providing that the direc-

tions given above are closely followed. This method was further tested by employing it for the determination of mercury in a sample of yellow mercuric oxide which had been analyzed by the sulphide method Weighed portions of the oxide were dissolved in 2 cc. of 1:1 nitric acid and the resulting solutions were diluted with 35 to 40 cc. of water and precipitated in the manner described above. The following results were obtained using a potassium iodate solution, 1 cc. equivalent to 0.00300 gram of mercury:

No	HgO Taken Gram	Cc. KIO_3 Required	Hg Found Per Cent	Hg by Sulphide Method Per Cent
1	0.1828	56 4	92 56	92 56
2	0 2215	68.3	92 57	92 63

In applying the method to the analysis of antiseptic tablets, a sample was prepared by grinding a dozen tablets to a fine powder. The portions taken for analysis were dissolved in 35 to 40 cc. of water and three drops of hydrochloric acid were added before the mercury was precipitated. In the case of the mercuric cyanide tablets which contained borax, it was necessary to add 1 cc. of

hydrochloric acid. The following results were obtained:

Preparation	Sample Grams	KIO_3 Used Cc.	$HgCl_2$ Found Per Cent	$HgCl_2$ by Sulphide Method Per Cent
$HgCl_2$, NH_4Cl	0 2358	27 85	47 96	47.97
	0 3623	42 80	47 97	48 00
Green $HgCl_2$, NH_4Cl	0 3428	39.25	46 49	46 50
	0 3313	27.95	46 51	46.44
Blue $HgCl_2$, citric acid	0 2024	39 25	63 49	63 64
	0 2551	39 95	63 59	63 51
			$Hg(CN)_2$	
Pink $Hg(CN)_2$, borax	0 2137	20 15	35 62	35.67
	0 3054	28 85	35 69	35 76

1 cc. of KIO_3 = 0 00300 gram of Hg, 0 004060 gram of $HgCl_2$, or 0 003778 gram of $Hg(CN)_2$

In the case of the green tablets, some of the dye was precipitated with the mercuric zinc thiocyanate and consequently a light green color was imparted to the chloroform indicator. However, by watching the color change in the chloroform, the end point of the titration was easily seen.

In order to dissolve basic mercuric salicylate it was found necessary to heat the portions taken

for analysis with 2 or 3 cc. of 1:1 nitric acid in covered beakers. When all was in solution, 40 cc. of water were added and the mercury was precipitated as soon as the solutions had cooled to room temperature.

No	Sample Gram	KIO_3 Used Cc	Hg Found Per Cent	Hg by Sulphide Method Per Cent
1	0.2040	38 30	56 32	56.31
2	0.2006	37.60	56 23	56 30
3	0 1876	35.15	56 21	—

Ammoniated mercuric chloride ($HgCl.NH_2$) was best dissolved by treating the portions taken for analysis with 5 cc. of hydrochloric acid. The mixture was allowed to stand for about half an hour with frequent shaking; then it was diluted with 5 cc. of water and heated just long enough to dissolve all of the substance. Immediately, 40 cc. of cold water was added, and when the solution was at room temperature, the mercury was precipitated as previously described.

The analyses given in the tables show that the iodate method gives very satisfactory results when applied to the examination of antiseptic preparations. It should be observed that in order

get satisfactory results, it is essential that the rections given should be followed in every ırticular.

The following results were obtained:

Sample Gram	KIO_3 Used Cc.	Hg Found Per Cent	Hg by Sulphide Method Per Cent
0 1709	45 5	79 87	79 86
0 1896	50 5	79 91	79 86
0 1757	46 7	79 79	—

In some cases it has been found that this ethod for the determination of mercury was the ly procedure which could be employed. For ample, Mr. J. L. Wiemer in his investigation the "Reduction in the Strength of the Merric Chloride Solution Used for Disinfecting veet Potatoes" (J. Agric. Res., *21*, 575-587 921)), found that this iodate method could be nployed satisfactorily because the colored subınces extracted from the sweet potatoes by the ercuric chloride solution did not interfere with e subsequent precipitation and titration of the ercury left in the solutions.

ANALYSIS OF ORGANIC MERCURY COMPOUNDS.

Many of these compounds can be sufficiently decomposed by treatment with concentrated nitric acid or aqua regia so that after the neutralization of the larger part of the free acid, the mercury can be precipitated and determined as already described by M. C. Hart and A. D Hirschfelder in their investigation of mercury compounds of phenyl carbinols (J. Am. Chem. Soc., *42*, 2678-2686 (1920). They employed this method for the determination of mercury with satisfactory results, but instead of titrating the mercuric zinc thiocyanate with potassium iodate it was filtered on a Gooch crucible, washed with the solution (5 cc. of precipitation reagent and 450 cc. of water) and dried to constant weight at 105° as recommended by the author in 1919.

0.2500 gram of $C_7H_6O_3Hg_2$ 3 $5H_2O$ gave 0 4138 gram $HgZn(SCN)_4 = 66.63$ per cent Hg, calc. 66.62 per cent.

0 2500 gram of $C_{18}H_{14}O_7Hg_2.H_2O$ gave 0.3556 gram $HgZn(SCN)_4$ = 57.26 per cent Hg, calc. 57.21 per cent.

0.2500 gram $C_9H_9O_6NHg$ gave 0.2916 gram $HgZn(SCN)_4$ = 46.95 per cent Hg, calc. 46.91 per cent.

0.2500 gram of $C_7H_7O_5NHg$ gave 0.3250 gram $HgZn(SCn)_4$ = 52.33 per cent Hg, calc. 52.02 per cent.

he Titration of Mercurous Chloride by Potassium Iodate.

It has been found that mercurous chloride ›acts with potassium iodate according to the ıeoretıcal requırements of the equatıon:

$$4HgCl + KIO_3 + 6HCl = 4HgCl_2 + KCl + ICl + 3H_2O$$

Portions of pure mercurous chloride which has ›en dried at 130 to 135° C. for several hours ere weıghed by difference from a specımen tube rectly into the glass-stoppered tıtration bottles. he titrations were made wıth the potassium date solution after the addition of 20 cc. of ater, 30 cc. of hydrochloric acid, and 6 cc. of ıloroform. The dried mercurous chloride reacts

more slowly than the precipitated compound which was titrated without drying in some experiments to be described beyond, so that in this case very thorough shaking is required throughout the titration. In some instances, it was found necessary to crush the residual lumps with a glass rod. The following results were obtained: (1 cc. of the potassium iodate solution = 0.01572 gram of HgCl):

No	HgCl Taken Gram	KIO_3 Used Cc	HgCl Found Gram	Error Gram
1	0 4999	31 80	0 4999	0 0000
2	0 5000	31 80	0 4999	—0 0001
3	0 5005	31 80	0 4999	—0 0006
4	0 6001	38 15	0 5997	—0 0004
5	0 4999	31 80	0 4999	0 0000

Since many kinds of organic matter do not interfere with this method of titration, it is applicable to various mixtures containing calomel. It was applied to calomel tablets containing milk sugar after pulverizing some of them to obtain a uniform mixture. Determinations of the mercurous chloride were also made by treating weighed portions of the pulverized tablets with

ɩter slightly acidified with hydrochloric acid d weighing the washed and dried insoluble ɪidue.

The following results were obtained:

Substance Taken Gram	KIO_3 Used Cc.	HgCl Found Per Cent
0.4811	16 50	53 91
0 6783	23.25	53.89
0 1976	Gravimetric	53 94
0 5694	"	54.00

The method was applied also to the determina-n of mercury in a mercuric compound by con-ting the latter into mercurous chloride which er filtration was titrated as described above. r this purpose weighed portions of mercuric loride were dissolved in warm water with the dition of a few drops of hydrochloric acid; an ess of phosphorous acid solution was then ded and after thorough stirring the precipitate s allowed to settle for about 12 hours. It was en collected on a filter paper and thoroughly shed with cold water. The precipitate with filter was put into the titration bottle, and y precipitate adhering to the beaker and stir-

ring rod was collected by wiping with a piece of filter paper and placed in the bottle. After the addition of 20 cc. of water, 30 cc. of hydrochloric acid, and 6 cc. of chloroform, the precipitates were titrated with a potassium iodate solution, 1 cc. = 0.013354 gram of Hg.

No.	$HgCl_2$ Taken Gram	KIO_3 Used Cc.	Hg Found Gram	Hg Present Gram	Error
1	0.3934	21 7	0.2898	0.2904	—0 0006
2	0.3107	17.2	0 2297	0.2294	+0 0003
3	0 4903	27 1	0 3619	0 3619	0 0000
4	0 3315	18 3	0 2444	0 2447	—0 0003
5	0 3407	18 8	0 2511	0.2515	—0 0004

These results show that the method gives satisfactory results when applied to the analyses of mercuric chloride.

THE DETERMINATION OF MOLYBDENUM.

This iodate method is based on the reduction f the molybdenum in a hydrochloric acid solu-ion by means of the Jones reductor. The re-luced solution is received directly from the eductor into a hydrochloric acid solution of odine monochloride and titrated in the usual nanner. The reaction which takes place may e represented by the following equation:

$$KIO_3 + Mo_2O_3 + 2HCl = Mo_2O_5 + KCl + ICl + H_2O$$

Jnlike the well-known permanganate titration, he iodate oxidized the molybdenum readily to Mo_2O_5 and further oxidation proceeded so slowly 2 to 3 days) that it was not practical to wait or it. It was found that a sharp end point was btained when the pentoxide was completely ormed. In order to test the method, a solution ontaining 3.567 grams of potassium iodate in 000 cc. was prepared and, according to the above

equation, 1 cc. = 0.003200 gram of Mo. For convenience a solution of ammonium molybdate was used. The solution was standardized by precipitating the molybdenum from measured volumes and weighing it as lead molybdate. It was found best to precipitate the molybdenum from a solution made slightly acid with nitric acid, with a solution of lead nitrate. After the solution was thoroughly stirred and the precipitate had settled for a few minutes, 5 cc. of a strong solution of ammonium acetate was added in order to be certain of obtaining a complete precipitation. This procedure gave a coarse, crystalline precipitate instead of a finely divided slimy one as is obtained when molybdenum is precipitated (as usually recommended) by lead acetate, in the presence of large quantities of acetates. Two analyses were made with the following results: 25.2 cc. of the solution gave 0.0989 gram of $PbMoO_4$, and 25 cc. gave 0 0973 gram, giving the value of 1 cc. respectively, 0.001022 and 0.001018 gram of Mo The average value 0.001020 was used.

The apparatus used for the reduction of the molybdenum consisted of a reductor (20 × 1.8 cm.) filled to within 3 cm. of the top with

30-mesh amalgamated zinc, which rested on a mat of glass wool about 2 cm. thick, which in turn was supported by a perforated platinum disk. The outlet of the reductor extended to within 1 cm. of the bottom of the titration bottle. The reductor was provided with a stopcock in order to be able to control the rate of reduction. A somewhat larger reduction tube should be used, is it was found that this one would not reduce he molybdenum completely unless the solution vas passed through very slowly. Previous to naking a reduction, 5 cc. of iodine monochloride solution, 25 cc. of hydrochloric acid, sp. gr. 1.18, cc. of water, and 7 cc. of chloroform were placed n one of the 500 cc. titration bottles. The bottle vas placed in a deep pan of cold water in order o cool the reduced solution rapidly. The reluctor was set up in another bottle, heated with ome dilute hydrochloric acid and about 100 cc. f hot water. When the water had run out, the eductor was transferred at once to the bottle in he cold water. A measured quantity of amnonium molybdate solution, acidified with 20 cc. f 1:1 hydrochloric acid, was heated to about 0° C., and passed very slowly through the reuctor, using gentle suction, directly into the

solution in the bottle. The bottle was frequently rotated gently so as to keep the solution thoroughly cooled and avoid any loss of iodine which separates as the reaction proceeds. After adding all of the solution the flask was rinsed with 1:2 hydrochloric acid several times and the washings were added to the reductor, which was further washed with about 50 cc. more of the acid. The exposure of the zinc during the reduction caused no error in the titration as would be the case with a permanganate titration because any hydrogen peroxide formed would not react either with iodine monochloride or potassium iodate, as has been found by direct experiments with hydrogen peroxide solution. When the washings had run through, the reductor was removed and the solution was titrated rapidly at first, then slowly, with thorough shaking with the glass stopper inserted after each addition of potassium iodate solution, until the chloroform indicator was decolorized, which marked the end point of the titration. If the solution became warm at all during the titration, it was important to cool it under running water. The bottle was placed in cold water for 5 minutes after the titration. If no more color appeared in the chloroform, the reaction was com-

pleted. It should be observed that when more than minute quantities of molybdenum are present, the solution has a rose or red color due to the molybdenum pentoxide. Several blank determinations were made using the same quantities of reagents and carrying out the entire procedure as in the actual experiments. It was found that the blank correction amounted to 0.05 cc. of the potassium iodate solution which has been deducted from each titration given below.

No	Cc of Mo Sol	Cc KIO_3 Used	Mo Found Gram	Mo Taken Gram	Error Gram
1	42 0	13 40	0 0428	0 0428	0 0000
2	41 9	13 25	0 0424	0 0427	—0 0003
3	29 9	9 55	0 0306	0 0305	+0 0001
4	20 5	6 35	0 0203	0 0204	—0 0001
5	32 5	10 30	0 0330	0 0332	—0 0002
6	46 0	14 70	0 0470	0 0469	+0 0001
7	34 9	11 00	0 0352	0 0356	—0 0004

Another series of experiments was made using weighed portions of molybdenum trioxide which were dissolved in ammonium hydroxide, then diluted to 20 cc. with water, acidified with 20 cc.

of hydrochloric acid, reduced and titrated. The following results were obtained:

No	MoO_3 Taken Gram	KIO_3 Used Cc.	MoO_3 Found Gram	Error Gram
1	0 0548	11 45	0 0549	+0.0001
2	0 0627	13 05	0 0626	−0.0001
3	0 0163	3 50	0 0168	+0.0005

The results show that molybdenum can be determined with accuracy by the iodate method. It should be observed that it is of importance to keep the solutions thoroughly cooled and in a shaded place during the titrations, especially if much molybdenum is present in order to obtain a sharp end point. During the titration it is important to maintain not less than 12 per cent of actual hydrochloric acid in the solution to prevent the hydrolysis of the iodine monochloride.

THE DETERMINATION OF HYDROGEN PEROXIDE.

The method is based upon adding a measured lume of hydrogen peroxide solution to an alka- e solution containing an excess of standard dium arsenite. When the reaction is com- eted concentrated hydrochloric acid is added d the unaltered arsenite is titrated with a undard potassium iodate solution using chloro- m as an indicator. The amount of arsenite und by titration is deducted from that taken, ing the quantity oxidized by the hydrogen roxide In order to obtain a quantitative re- ion with the hydrogen peroxide and the dium arsenite, it was found necessary to employ excess of sodium hydroxide as directed below. should be observed that this procedure is not luenced by the presence of organic preserva- es as is the case with the well-known per-

manganate method. The following equations represent the reactions which take place:

$$As_2O_3 + 2H_2O_2 = As_2O_5 + 2H_2O$$

$$As_2O_3 + KIO_3 + 2HCl = As_2O_5 + KCl + ICl + H_2O$$

In order to test the method, a solution containing 3.567 grams of potassium iodate in 1000 cc. was used. The tenth normal sodium arsenite was prepared by dissolving 4 948 grams of pure arsenious oxide in 50 cc. of water which contained 4 grams of sodium hydroxide. When the arsenious oxide had dissolved, 200 cc. of a saturated solution of sodium bicarbonate was added along with enough water to make 1000 cc. The relationship between the arsenite and iodate solutions was obtained by titrating a measured volume of the arsenite solution acidified with two-thirds volume of hydrochloric acid. Five cubic centimeters of the sodium arsenite solution were found equivalent to 7.5 cc. of the iodate solution or 1 cc. of KIO_3 = 0.667 cc. of As_2O_3 If desired the relationship of the two solutions may be calculated as follows: 1 cc. of KIO_3 = 0 003297 gram of As_2O_3 ÷ 1 cc. of As_2O_3 = 0 004948 gram of As_2O_3 = 0.667 cc. of the arsenite solution which is

identical with the result obtained by actual titration.

The hydrogen peroxide solution employed to test the method was made by diluting 50 cc. of ordinary commercial peroxide to 500 cc. Measured volumes of the arsenite solution which must be in excess of that required by the hydrogen peroxide taken for analysis, were placed in the glass stoppered titration bottles along with 10 cc. of a 10 per cent solution of sodium hydroxide. A measured volume of the hydrogen peroxide solution was added from a buret while the contents of the bottle were gently rotated. After the solution had stood for 2 minutes, 40 cc. of hydrochloric acid were cautiously added. The stopper was inserted, and while holding it firmly in place, the bottle was violently shaken in order to separate as much carbon dioxide as possible from the solution. Then the stopper was carefully released so as to allow the excess pressure of gas to escape without losing any solution. After adding 6 or 7 cc of chloroform, the unoxidized arsenite was titrated with the potassium iodate solution. The iodate solution required for the titration was converted into its equivalent of arsenite solution which was deducted from that

originally taken, leaving that oxidized by the hydrogen peroxide. One cubic centimeter of the As_2O_3 solution was equivalent to 0 001701 gram of H_2O_2. The following results were obtained:

No.	H_2O_2 Sol. Cc. Taken	N/10 As_2O Sol Cc Taken	KIO_3 Used Cc.	As_2O_3 Sol. Oxidized by H_2O_2 Cc	H_2O_2 Found Gram	By Kingzett Method Gram
1	15 1	34.9	4 90	31 60	0 0537	—
2	15 0	34 9	5 02	31 55	0 0536	0 0539
3	20.0	46 0	6 00	42 00	0 0714	0 0710
4	20 0	45 5	5 45	41 90	0 0712	—
5	22 0	49 9	5 90	46 00	0.0782	0 0781
6	22 0	49 9	5.90	46 00	0.0782	0 0781

It should be noted that the titrations were made during a period of three hours after the preparation of diluted hydrogen peroxide solution. It is important to titrate the hydrogen peroxide solution, which has been diluted with distilled water of the laboratory soon after dilution because it was found the hydrogen peroxide gradually decomposed. The results reported in addition to other similar experiments show that the method gives accurate results. In practice it is

recommended that a fifth normal solution of sodium arsenite along with an equivalent potassium iodate solution (10.700 grams of KIO_3 per 1000 cc.) should be used for this determination. The sodium arsenite solution prepared as already described has excellent keeping qualities. A solution well over a year old had not changed sufficiently to be detected.

THE DETERMINATION OF SULPHUROUS ACID.

The method is based on the titration of sulphurous acid with potassium iodate in the presence of 15 to 20 per cent of actual hydrochloric acid, using chloroform as an indicator. In order to test the method, a solution containing 3.567 grams of potassium iodate in a 1000 cc was used. According to the equation $KIO_3 + 2H_2SO_3 + 2HCl = 2H_2SO_4 + ICl + KCl + H_2O$ the equivalent of this solution is 1 cc. = 0.002135 gram of SO_2. Measured quantities (5-20 cc.) of sulphur dioxide solutions which had recently been titrated by the Giles-Shearer method (J. Soc. Chem. Ind. *3*, 197, and *4*, 303) were placed in the titration bottles. To each was added a thoroughly cooled mixture of 30 cc. of hydrochloric acid and 20 cc. of water along with 6 cc. of chloroform. During the first part of the titration the potassium iodate solution was added rapidly while shaking the bottle so as to give the con-

tents a rotary motion, until the iodine which is liberated has largely disappeared from the solution. Then the stopper is inserted and the solution is shaken. From this point the titration is continued with thorough shaking of the closed bottle after each addition of the potassium iodate solution until the end point is reached. The following results were obtained:

No	SO_2 Taken Gram	KIO_3 Used Cc.	SO_2 Found Gram
1	0.0224	10 53	0 0225
2	0 0290	13 70	0 0292
3	0 0290	13 72	0 0293
4	0 0315	14 85	0 0317
5	0 0317	14 95	0 0318
6	0 0628	29 70	0 0634

The following results were obtained by titrating measured quantities of a sodium bisulphite solution:

SO_2 Taken Gram	KIO_3 Used Cc	SO_2 Found Gram
0 0495	23 40	0 0499
0 0492	23 20	0 0495
0 0492	23 15	0 0494
0 0328	15 40	0 0329
0.0336	15 70	0 0335

It was found important to cool the hydrochloric acid solution to 18° C. before adding it to the sulphite solution. When it is desired to titrate much larger quantities of sulphite, it is recommended that the sulphite should be added to a titration bottle which contains 10 to 15 cc. of iodine monochloride solution in addition to the usual amount of hydrochloric acid. The iodine monochloride reacts with the sulphite and prevents the loss of any sulphite. The liberated iodine is titrated with potassium iodate in the usual manner. The use of iodine monochloride does not change the sulphur dioxide equivalent of the potassium iodate solution. The iodine monochloride solution is prepared as follows: Dissolve 10 grams of pure potassium iodide and 6.44 grams of potassium iodate in 75 cc. of water, add 75 cc. of hydrochloric acid, then add 5 cc of chloroform in a glass stoppered bottle, and adjust exactly to a very faint iodine color (chloroform) by shaking and adding a dilute solution of potassium iodide or iodate, as the solution may require. This solution should be kept in a very dark place when not being used.

Several experiments were made by adding weighed portions of sodium bisulphite to hydro-

›ric acid solutions to which iodine-mono-›ride had been added as described above, and ›r shaking the solutions, they were titrated h potassium iodate with the following results:

Wt of ‑INaSO$_3$ Gram	KIO$_3$ Used Cc.	SO$_2$ Found Per Cent	SO$_2$ Present Per Cent
0 0972	26 35	57.88	58 01
0 1271	34 56	58 04	58.01
0 1392	37 85	58.05	58 01
0 1372	37.25	57 96	58 01

ʋas found preferable to weigh the sulphite in rt specimen tubes and after dropping them ›fully into the titration bottles quickly to ›rt the stoppers so as to avoid the loss of ›hur dioxide.

'he iodate method has been successfully ap-›d to the analysis of sulphites and the deter-ıation of sulphur dioxide in gaseous mixtures Percy Haller (J. Soc. Chem. Ind. 1919, *38*, 52 ›6 T). The author found that by adding 5 cc. glycerine per 100 cc. of caustic soda solution d to absorb the sulphur dioxide from the gase- mixtures, the sulphite remained entirely unoxi-›d, which was not the case in similar solutions

which contained no glycerine. He found that the passage of air and heating the solution had no effect on the sulphite in the presence of glycerine. The glycerine, if pure, does not interfere with the accuracy of the iodate titration. Mr. Haller stated that he did not find it necessary to use iodine monochloride in the titration of sulphites by the iodate method.

THE DETERMINATION OF SODIUM THIOSULPHATE.

̣odium thiocyanate has been found to react ̣h potassium iodate in the presence of strong ̣lrochloric acid according to the following ̣ıatıon:

$$2KIO_3 + Na_2S_2O_3\ 5H_2O + 2HCl = \\ Na_2SO_4 + K_2SO_4 + 2ICl + 6H_2O$$

n order to test the method several solutions sodium thıosulphate were prepared and stand- ̣lized by tıtration wıth known quantıties of ̣e iodıne ın the usual manner. Measured umes of these solutions were placed in the) cc. glass-stoppered tıtration bottles and 30 cc. hydrochlorıc acıd which had been cooled to ̣ut 18° C. was added. It ıs ımportant to titrate soon as possible after the thiosulphate is ̣ught in contact with the acıd. The following ults were obtained wıth a potassium iodate

THE DETERMINATION OF TETRATHIONATES

Tetrathionates can be readily titrated in the same manner as thiosulphates, except that it is not necessary to take precautions about cooling the hydrochloric acid before it is added to the solution of the tetrathionate. The reaction between sodium tetrathionate and potassium iodate in the presence of strong hydrochloric acid is as follows:

$$2Na_2S_4O_6 + 7KIO_3 + 10HCl =$$
$$4H_2SO_4 + 2Na_2SO_4 + K_2SO_4 + 7ICl + 3KCl$$

The following titrations were made with an iodate solution which had the value—1 cc. = 0.003297 gram of $Na_2S_4O_6$:

No	Wt of $Na_2S_4O_6$ Gram	KIO_3 Used Cc	Wt Found Gram	Error Gram
1	0 0640	19 35	0 0638	—0 0002
2	0 0766	23 20	0 0765	—0 0001
3	0 1373	41 70	0 1375	+0.0002
4	0 0872	26 43	0 0871	—0 0001
5	0 1065	32 30	0 1065	0 0000
6	0 0880	26 80	0 0884	—0.0006

solution, 1 cc. of which was equivalent to 0.005300 gram of $Na_2S_2O_3\ 5H_2O$.

No	$Na_2S_2O_3\ 5H_2O$ Gram Taken	KIO_3 Used Cc	$Na_2S_2O_3\ 5H_2O$ Gram Found	Error Gram
1	0 0847	16 00	0 0848	+ 0 0001
2	0 1008	19 00	0 1007	— 0 0001
3	0 0613	11 60	0 0614	+ 0 0001
4	0 0413	7 80	0 0413	0 0000
6	0 1554	29 35	0 1555	+ 0 0001
7	0.2051	38 70	0 2051	0.0000
8	0 2430	45 95	0 2435	+ 0 0005
9	0 1923	36 30	0 1924	+ 0 0001

The results given above show that the method is accurate. Care should be taken as in the case of all iodate titrations that sufficient hydrochloric acid is used so that at least 12 per cent of actual acid is present at the end of the determination. This method is employed to standardize thiosulphate solutions.

Dithionates were found to react so slowly with potassium iodate in the presence of hydrochloric acid that it was possible to titrate and determine the quantity of sodium thiosulphate in the presence of dithionates. Likewise tetrathionates could be estimated in mixtures with dithionates. It was found that barium and sodium dithionates were only partially decomposed by potassium iodate after reacting for a day and no iodine was liberated for some time after these substances were brought together.

THE DETERMINATION OF TIN.

The method is based upon the titration of precipitated tin or stannous chloride with potassium iodate in the presence of strong hydrochloric acid. This method has the advantage over others in that the end point is exceedingly sharp. Furthermore, there is far less danger of over titrating the solution. Another advantage is that extreme precautions to prevent outside oxidation of the tin during the titration are not necessary because the potassium iodate solution may be added very rapidly to the appearance of iodine in the solution, then without further precaution the titration can be completed as slowly as desired. It should be observed that the iodate method can not be employed to titrate tin or stannous chloride in the presence of antimony, cuprous ferrous salt or precipitated metals. However, in most cases, it is a simple matter to avoid or eliminate these interfering substances and apply the method with satisfactory results.

In order to test the method, a solution containing 3.567 grams of potassium iodate in 1000 cc. was used. According to the equations

$$KIO_3 + Sn + 6HCl = SnCl_4 + KCl + ICl + 3H_2O$$

$$KIO_3 + 2SnCl_2 + 6HCl = 2SnCl_4 + KCl + ICl + 3H_2O$$

the equivalents of this solution are respectively 1 cc. = 0 001983 gram Sn and 0.003966 gram Sn. The titrations were conducted in the usual 250 cc. glass-stoppered bottles in the presence of 30 cc. hydrochloric acid, 20 cc. of water, and 6 cc. of chloroform. During the first part of the titration, the potassium iodate was added rapidly while shaking the bottle so as to give the contents a gentle rotary motion until the iodine color, which gradually appeared, had increased to the maximum amount, then the stopper was inserted and the solution was thoroughly shaken. The titration was continued with thorough shaking of the closed bottle after each addition of potassium iodate solution until the end point was obtained.

The first experiments were made using a solu-

ɔn of stannous chloride which was prepared by luting 50 cc. of the laboratory reagent to one er. This solution contained 225 cc. of 1: 1 hy-ochloric acid which was sufficient to maintain perfectly clear solution. This solution was ındardized by the iodine method on three dif-rent days as indicated in the table below. No ecautions were taken to prevent the oxidation the stannous chloride and it was observed that e more solution removed from the liter flask, e faster the stannous chloride was oxidized by e oxygen of the air admitted to the flask, as ɔuld naturally be expected. The following re-lts were obtained:

Date May, 1916	$SnCl_2$ Sol Cc	KIO_3 Used Cc	Sn (as $SnCl_2$) Present By Iodine Gram	By Iodate Gram
14	10 0	16 0	0 0636	0 0635
17	10 0	14 9	0 0595	0 0591
17	10 0	15 0	0 0595	0 0595
18	10 0	14 8	0 0587	0 0587

will be observed that the iodate titrations ıecked the iodine titrations closely. The iodate ethod will be found very convenient to deter-ine the quantity of stannous chloride present

in solutions. In cases where it is necessary to titrate considerable quantities of stannous chloride, it is recommended that a much stronger solution of potassium iodate be employed, as it is very important to have the solution at the end of the titration contain at least 12 per cent of actual hydrochloric acid to prevent the hydrolysis of the iodine monochloride.

For the next series of experiments, a standard solution was prepared by dissolving exactly 3 grams of pure tin in about 150 cc. of hydrochloric acid, with enough nitric acid to oxidize the tin to stannic chloride. Three grams of tartaric acid were added and the solution was diluted to one liter. Measured portions of this solution were placed in titration bottles, in each of which was placed 2 grams of high grade 30-mesh zinc. After the reaction had proceeded for 20 minutes or longer, 40 cc. of 1: 2 hydrochloric acid was added. As soon as the zinc had completely dissolved leaving metallic tin, several cc. of potassium iodate solution were added, followed by 10 cc. of hydrochloric acid, and a piece of platinum foil to facilitate the solution of the tin. The titration was continued with very thorough shaking until the tin was practically all dissolved. Then 6 cc

chloroform were added and the titration fin-
ıed in the usual manner. It is very important
rıng the tıtration to add sufficıent potassium
late so that there is free iodine or iodine mono-
loride present in the solution at all times,
ıerwıse some of the tın might dissolve, form-
ʒ stannous chloride and hydrogen and thus
use a serious error. A blank determination
ing 2 grams of zinc and the same quantity of
drochlorıc acid as in the actual titrations re-
ired 0.40 cc. of potassium iodate solution which
s been deducted from the amounts of solution
KIO_3 used) in the following table:

KIO_3 Used Cc.	Tın Present Gram	Tın Found Gram	Error Gram
15 00	0 0300	0 0297	—0 0003
30 40	0 0600	0 0601	+0 0001
7 60	0 0150	0 0151	+0 0001
30 20	0 0600	0 0599	—0 0001
24 00	0 0476	0.0478	+0 0002
20 95	0 0420	0 0416	—0 0004
45 40	0 0900	0 0902	+0 0002

ese results show excellent agreement with the
antities of tin present, thus confirmıng the

equation given above. The solution of tin even in the presence of platinum was slow and it was found that a titration required from one half to three-quarters of an hour for completion.

Since it appeared that nickel would be the most suitable reducing agent for general use with the iodate method, the next series of experiments was made using strips ($1 \times 5.5 \times 0.1$ cm.) of sheet nickel for the reduction, which was found satisfactory. The reduction was made in 250 cc Erlenmeyer flasks provided with a 2-hole rubber stopper which carried a glass tube extending to within 1 cm. of the surface of the liquid. The other hole was provided with a short tube which extended a short distance below the stopper. Several experiments were made using measured portions of the stannic chloride solution described above. To each portion of this solution 15 cc of hydrochloric acid and 2 nickel strips were added. The stopper was inserted and the flask was heated on the steam bath for 45 minutes to insure complete reduction of the tin. Then a current of carbon dioxide was passed through the longer tube and the flask placed in ice water. When the solution had reached approximately the

temperature of the bath, it was filtered by suction into a titration bottle (containing 6 cc. of chloroform) to remove the finely divided nickel which had separated from the edge of the strips. The filter used was a calcium chloride prolong tube (10 × 1.8 cm.), provided with a perforated

Reduction by Sheet Nickel and Titration of Stannous Salt

No	$SnCl_4$ Taken Cc	KIO_3 Used Cc	Tin Present Gram	Tin Found Gram
1	30.0	22.77	0.0900	0.0900
2	21.0	15.80	0.0630	0.0627
3	18.0	13.60	0.0540	0.0539
4	10.0	7.55	0.0300	0.0299
5	9.9	7.40	0.0297	0.0294
6	10.0	7.50	0.0300	0.0298
7	10.0	7.50	0.0300	0.0298

platinum disk upon which was placed a thin layer of absorbent cotton, a layer (2.5 cm.) of purified sea sand, and another thin layer of cotton on top. Other filter mediums were tried but were not found satisfactory. Before pouring the solution into the filter, a moderate stream of car-

bon dioxide gas was led in by means of a be glass tube which extended to within 1 cm of t filter bed for a minute after starting the suctic The flask and filter were washed with small qua tities of 1:1 hydrochloric acid and the soluti was titrated at once. It was found necessary make blank determinations under the very san conditions as in the actual experiments with ea new lot of sheet nickel and apply the correctio (due to the iron content of the nickel) to tl subsequent titrations. The results in the tab given above include this correction, amounting 0.5 cc. of potassium iodate solution.

Determination of Tin in Solder and Type Metal

In order to apply this method to the dete mination of tin in these alloys, a sample of 0 to 0 5 gram, depending upon the quantity of t present, was heated in a 250 cc. Erlenmeyer flas with 15 cc. of concentrated sulphuric acid. is very important to boil the solution gently unt all sulphur dioxide is expelled, otherwise it woul be titrated along with the tin. After coolin 20 cc. of water and 15 cc. of hydrochloric aci were added, after which the tin was reduced an

titrated as described above. The following results were obtained:

No	Sample	Alloy Taken Gram	KIO_3 Used Cc	Grav. Det Per Cent	Tin Found Per Cent
1	Type metal.	0 5000	6 30	5 04	4 99
2	" " ..	0 5000	6 25	5 04	4 96
3	" " .	0.5000	3 90	3 20	3 09
4	" " .	0 5000	4 00	3 20	3 17
5	Solder ...	0 2000	19 60	38 76 [a]	38 86

[a] Iodine method

It is recommended that a potassium iodate solution containing 8.994 grams of KIO_3 per liter (1 cc. = 0.01000 gram Sn) should be used for the analysis of solders, using a 0 5 gram sample. It should be observed in the analysis of type metals, etc., that when the filter becomes clogged with precipitated antimony, it should be heated with warm nitric and tartaric acids and washed thoroughly with water until all of the antimony is removed. Also it is advisable to keep the nickel strips free from deposited metals by frequent cleaning.

Determination of Tin in Bronze and Other Alloys.

Alloys containing copper are best decomposed in the usual manner with nitric acid The metastannic acid is filtered on a Gooch crucible. After washing the precipitate, it was transferred along with the asbestos mat to a 250 cc. Erlenmeyer flask, any precipitate adhering to the sides of the crucible being removed with a pinch of slightly damp asbestos and added to that in the flask. About 15 cc. of concentrated sulphuric acid were added and the flask was heated until the acid had boiled gently for 2 or 3 minutes. After cooling thoroughly 20 cc. of water and 15 cc. of hydrochloric acid were added. The asbestos was filtered on a Gooch crucible and washed with 1:1 hydrochloric acid, using as little as possible. Then the solution was reduced with nickel and titrated. An analysis of a bronze gave the following results:

Alloy Gram	KIO_3 Used Cc	Tin by Grav Det. Per Cent	Tin Found Per Cent
0.5000	10.95	8.75	8 68
0 5000	10 93	8 75	8 66
0 5000	11.05	8.75	8.76

The results given in the above tables show that the iodate method is applicable to the satisfactory determinations of tin in alloys of various kinds.

THE DETERMINATION OF ZINC

This method is based upon the precipitation of zinc in neutral or acid solutions by a reagent which contains 39 grams of ammonium or potassium thiocyanate and 27 grams of mercuric chloride per liter. The precipitate of zinc mercuric thiocyanate is filtered and titrated with potassium iodate solution in the presence of strong hydrochloric acid and chloroform indicator. The reaction which takes place is according to the following equation:

$$ZnHg(SCn)_4 + 6KIO_3 + 12HCl \quad ZnSO_4 + HgSO_4 + 2H_2SO_4 + 6ICl + 4HCn + 6KCl + 2H_2O$$

In order to get a quantitative precipitation of the zinc mercuric thiocyanate there should not be more than 5 per cent of free acid present in the solution before the addition of the precipitating reagent. Also it should be observed that in cases where larger quantities of acid are

required for the solution of a substance, the excess of acid should be neutralized with sodium hydroxide instead of ammonia, because an excessive quantity of ammonium salts exerts a solvent action upon the precipitate of the double thiocyanate. In applying this method it should be observed that bismuth cadmium, cobalt, copper, manganese, and mercurous compounds give insoluble double thiocyanates. Nickel in small quantities does not interfere appreciably with the method. When appreciable quantities of ferric compounds are present, it is best to reduce them with sulphur dioxide, otherwise some ferric thiocyanate is carried down with the zinc precipitate.

In order to test the method two solutions were prepared from Kahlbaum's purest zinc sulphate. They were standardized by the well-known phosphate method. Measured volumes of these solutions were taken in perfectly cleaned small beakers. Each solution was treated with 25 cc. of the precipitating reagent described above and 20 cc. of water. The solutions were vibrated by striking the sides of the beakers with a stirring rod to facilitate the separation of the crystals. After the solutions had stood for about 5 minutes, they were briskly stirred with a glass rod previ-

ously moistened with water, for about a minute This treatment permitted the rod to be easily rinsed free from the precipitate so that it could be removed from the solution. In all cases, the solutions were allowed to stand at least an hour before filtration. The precipitates were collected on 7 cm. filter papers placed in small Hirsch porcelain funnels using gentle suction and were washed four or five times with a solution which contained 5 cc. of the mercuric thiocyanate reagent and 450 cc. of water. When the filters had drained, the filter papers containing the precipitates were carefully removed and folded so that they could be placed in the titration bottles. A thoroughly cooled mixture of 35 cc. of hydrochloric acid and 10 cc. of water along with about 7 cc. of chloroform was added to one of the titration bottles containing the zinc mercuric thiocyanate, because it is best to titrate immediately after the addition of the acid. During the first part of the titration, the potassium iodate solution is added rapidly while rotating the bottle in order to keep the contents mixed. When the iodine which is liberated during the first stage of the reaction has disappeared from the solution, the stopper is inserted and the con-

tents of the bottle are thoroughly mixed by shaking for about half a minute. From this point the titration is continued slowly, shaking the closed bottle thoroughly after each addition of potassium iodate until the iodine color has disappeared from the chloroform indicator which marks the end point. If more than 50 cc of the potassium iodate solution is required for a titration, 10 to 15 cc. more of hydrochloric acid should be added before continuing the titration, in order to prevent the hydrolysis of the iodine monochloride. The following results were obtained using a solution which contained 39.2882 grams of potassium iodate in 1000 cc. and 1 cc. was equivalent to 0.002000 gram of zinc.

No	Zinc Taken Gram	KIO_3 Cc.	Zinc Found Gram
1	0 0925	46 15	0 9230
2	0 1007	50 35	0 1007
3	0 0822	41 00	0 0820
4	0 1028	51 20	0 1024
5	0 0411	20 55	0 0411
6	0 0966	48 15	0 0963
7	0 0616	30.75	0 0615
8	0 0493	24 60	0 0492

The Determination of Zinc in Commercial Zinc Arsenite.

Weighed portions were dissolved in 3 cc. of hydrochloric acid. About 10 cc. of strong sulphur dioxide water was added and the solutions were heated upon the steam bath until the odor of sulphur dioxide had largely disappeared. This treatment was made to reduce the ferric chloride because it was previously found that there was enough iron in these samples to give the precipitated zinc mercuric thiocyanate a strong color which could not be removed by washing. When the heated solutions had cooled to room temperature 25 cc. of the precipitating thiocyanate reagent was added and the analyses were conducted as described above. The following results were obtained: 1 cc. of KIO_3 Sol. = 0.002489 gram of ZnO.

No	Zinc Arsenite Gram	KIO_3 Used Cc.	ZnO Found Per Cent	ZnO by Phosphate Method Per Cent
1	0 2146	48 00	55 67	55 66
1	0 2578	56 30	55 65	—
2	0 1607	35 90	55 60	55.59
2	0 2110	47.15	55 62	—

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ATOMIC WEIGHTS (1923).

Antimony	120.20
Arsenic	74.96
Cadmium	112.40
Chlorine	35.46
Chromium	52.00
Cobalt	58.97
Copper	63.57
Hydrogen	1.008
Iodine	126.92
Iron	55.84
Manganese	54.93
Mercury	200.60
Molybdenum	96.00
Nickel	58.68
Nitrogen	14.01
Oxygen	16.00
Phosphorus	31.04
Potassium	39.10
Silver	107.88
Sodium	23.00
Sulphur	32.06
Tin	118.70
Zinc	65.37

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